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N-SUBSTITUTED MELAMINES

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5 Claims. (Cl. 260—249.6)

This is a divisional application of application Ser. No. 208,105, filed July 6, 1962, now abandoned.

The present invention concerns N-substituted melamines which are useful as synthetic lubricating agents and/or as hydraulic liquids.

Very high demands with regard to heat stability are made of synthetic lubricating agents and hydraulic liquids such as are necessary, for example, in turboprop aero engines or the modern high temperature apparatus in mechanical and electrical industries.

For use in turboprop aero engines, synthetic lubricating agents must, in the first place, fulfill the following conditions:

(1) They must be capable of forming a lubricating film on the most various metals;
(2) They must be only slightly volatile and have substantial stability to heat;

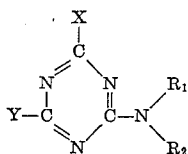
(3) They should not have a corrosive action and, above all, they should not form acid decomposition products;

(4) They should retain their lubricating properties over as wide a temperature range as possible, i.e. their viscosity should be as little dependent as possible on temperature;

(5) They should have, in addition to these properties, on the one hand as low a solidification point as possible and on the other as high a boiling point as possible.

It is difficult to find substances which fulfill these demands to such an extent that they can be employed, for example, as lubricants for turboprop aero engines. The usual lubricants do not fulfill the demands of modern motors, in particular of turboprop aero engines; those of an ester basis because of their volatility and heat stability and those of a hydrocarbon basis because of their volatility, their solidification point and the dependence of their viscosity on temperature (ASTM slope).

It has now surprisingly been found that certain melamines suitably substituted at the nitrogen atom of the amino groups have the properties required above and thus can be used as hydraulic liquids when high demands are made and as synthetic lubricants for a particularly wide range of temperatures. The melamines usable according to the invention are compounds of the formula:



(1)

wherein

X is a di-lower alkyl-amino group in which each alkyl radical has from 2 to 4 carbon atoms

Y is a di-lower alkyl-amino group in which each alkyl radical has from 2 to 4 carbon atoms

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R₁ is hydrogen or lower alkyl of maximally 4 carbon atoms,

R₂ is benzyl, phenyl, alkylphenyl wherein alkyl has maximally 12 carbon atoms, alkoxy-phenyl, wherein alkoxy has maximally 4 carbon atoms or phenoxy-phenyl.

Very interesting as lubricants on account of their good ASTM-slope which is below 0.8 are the compounds of the above Formula I in which there are a total of four alkyl substituents as well as one aromatic or araliphatic substituent at the three amino nitrogen atoms, the araliphatic substituent being preferably a benzyl group.

Another sub class of compounds which are particularly interesting in view of their good lubricant properties (ASTM slope in the order of 0.7 or lower, and high heat resistance expressed by a weight loss at 380° C. below 6%) are those compounds of the above Formula I in which these are a total of five substituent alkyl groups and one aromatic group at the three amino nitrogen atoms and wherein the aromatic group is preferably a phenyl group.

Apart from substituted, particularly aryl- and alkyl-substituted amino groups, the nitrogen substituents of melamines usable according to the invention must not contain any functional groups. In particular they contain no acid, salt-forming substituents or any which can be converted into such; for example they contain neither sulphonic acid groups nor carboxyl, sulphonic acid ester, carboxylic acid ester, sulphamyl, carbamoyl nor cyano groups.

The N,N,N'-substituted melamines used according to the invention, are easily produced by reacting in steps, by known methods, the three chlorine atoms of cyanuric chloride with primary or secondary organic amines.

In the first and/or second step, less easily reacting amines are reacted and in the third step those which react easily are reacted. The reaction is performed advantageously in inert organic solvents and diluents such as low aliphatic ketones, aliphatic or alicyclic ethers such as dibutyl ether, tetrahydrofuran or dioxan, or aromatic hydrocarbons or halogenated hydrocarbons such as benzene, toluene, xylene or dichlorobenzene, in the presence of acid binding agents at suitable temperatures. Examples of acid binding agents are the alkali metal salts of low fatty acids such as sodium acetate, also those of weaker polybasic acids such as sodium or potassium carbonate, sodium or potassium hydrogen carbonate and, in suitable amount and form, also alkali hydroxides as well as tertiary nitrogen bases such as triethylamine, triethanolamine, pyridine etc. The first chlorine atom of the cyanuric chloride is reacted advantageously at low temperature up to 15° C., the second chlorine atom is reacted at medium temperatures up to 60° C. and the third chlorine atom is reacted, if necessary, at higher temperatures, an excess of the amine being used advantageously as acid binding agent. Aliphatic amines which can be used, for example, are primary and secondary amines containing normal and/or branched chain alkyl groups of 1 to 6 carbon atoms or alkoxyalkyl groups of 3 to 12 carbon atoms, or aminoalkyl groups having advantageously a tertiary amino group, e.g. a dialkylamino, diaralkylamino, dicycloalkylamino, alkylaralkylamino, alkylarylaminio, polymethylenimine, morpholino or N'-alkylpiperazino group.

Examples of primary aromatic amines are aniline, chloro bromo- aniline, alkylanilines such as toluidines, xylidines, t-butyl or t-amyl anilines, aminotetrahydronaphthalenes, aminodiphenyls, aminodiphenylalkanes,

aminodiphenylamines, aminodiphenyl ethers, aminodiphenylthioethers and secondary amines of this series such as compounds alkylated, aralkylated or alicyclically substituted at the amino nitrogen atom.

The N,N',N''-substituted melamines according to the invention can contain mixtures of primary, secondary and tertiary amines. Because of their great stability to heat, they can easily be obtained in pure form by distillation. The melamine derivatives can also be purified by extraction with a selective solvent such as acetic acid, by treatment with a bleaching earth such as Tonsil AC or an adsorption each such as Celite FC or with an ion-exchanger such as Amberlite IR 120.

The N,N',N''-substituted melamines used according to the invention are only slightly volatile oils or of fatty or wax-like consistency and they are distinguished by high thermostability as they decompose only at temperatures over 380° C. In this respect they have the advantage over the best products used up to now for this purpose, namely the triesters of higher fatty acids with trimethylolpropane; these cannot be used at temperatures of over 320° C. In addition, the lubricants and hydraulic liquids according to the invention are more stable to hydrolysis than lubricants of an ester basis used up to now.

Also, even under extreme test conditions such as are laid down for turboprop aero engines, they hardly form any acid decomposition products. Thus, for example, the volatile compounds formed from 2,4-bis-dibutyl amino-6-p-phenoxyphenyl-1,3,5-triazine (compare compound No. 3 in the following Table I), and also the residue have an acid value of only 1 mg. KOH/g. or 0.7 mg. KOH/g. respectively after 6 hours' exposure to a temperature of 380° C., i.e. both the volatile compounds as well as the residue formed from compound No. 3 of Table I are neutral for all practical purposes after several hours exposure to heat whereas the volatile substances formed from trimethylolpropane tripelargonate under the same conditions have an acid value of 117.3 mg. KOH/g.

In addition, the flash point of the melamines usable according to the invention is favorable. It was determined according to the ASTM designation: D 93-58 T (The American Society for Testing Materials, 1915 Race St., Philadelphia 3, Pa.). In the case of compound 3 of Table I mentioned above, it is 300° C. and is thus higher than that of the sebacates of alkanols.

The melamines according to the invention are distinguished over the previously known substances recommended as lubricants for turboprop engines such as e.g. the ortho-phosphoric acid esters of organic hydroxyl compounds, by their much slighter corrosive action; they are distinguished over the esters of higher polycarboxylic acids with polyalcohols by their swelling action on synthetic materials such as, e.g. on higher molecular copolymers from butadiene and acrylonitrile (e.g. HYCAR 38, made by Messrs. Goodrich in Akron, Ohio; U.S.A.); and they are distinguished over esters from pentaerythrite ad monocarboxylic acids of medium chain length by considerably less separation out of resinification and carbonisation products. They are distinguished over all these known lubricants in that they are very stable particularly at high temperatures. In addition, they are distinguished over the silicone oils, some of which are also thermostable, by their better lubricating properties. The very good stability to acid and alkali of the melamine derivatives used according to the invention is also remarkable. In the liquid state, these melamine derivatives have medium to high viscosity.

The melamines usable according to the invention can be employed as lubricants in many ways. Properties desirable for a particular purpose can also be attained by the production of suitable mixtures of these melamines.

Thus, the melamines usable according to the invention are suitable for the lubrication of hard surfaces because, on contact with these surfaces, they form very adhesive

surface films, e.g. they are suitable for lubricating the surface of metals as well as alloys thereof, the surfaces of silicates such as, e.g. glasses as well as of other materials needing lubrication such as, e.g. rubber washers.

The N,N',N''-substituted melamines usable according to the invention can be employed alone or they can also contain additives. Thus, when they are to be used at temperatures of over 150° C., to make use of their favourable stability to heat they are mixed advantageously with antioxidants in order to hinder the auto-oxidation which sets in above this temperature. In this case, the amount of antioxidants is about 0.01 to 5% of the melamines.

Mono- or hetero-cyclic aromatic amines, hydroxyl-substituted aromates, aminohydroxyaryl compounds as well as certain heterocyclic compounds can be used as antioxidants.

Of the amines, usable as antioxidants, in general the secondary monoamines, particularly the diarylamines having homo- and hetero-cyclic radicals as well as the aromatic diamines, the amine substituents, preferably secondary, of which are in the ortho or, advantageously the para-positions are particularly valuable.

Examples of homocyclic and heterocyclic aromatic diarylamines usable as antioxidants, are diphenylamines, phenylnaphthylamines, phenylacenaphthenylamines; 4,4'-dinaphthylaminodiphenyl; thiazolyl - (2) - naphthylamines; example of aromatic diamines are N,N'-diphenyl-p-phenylenediamine, N,N'-dioctyl - p - phenylenediamine, phenyl-p-phenylenediamine, N,N'-bis-(γ -aminopropyl-p-phenylenediamine.

Of the hydroxyl-substituted aromates usable as antioxidants which are employed particularly at not too high temperatures (i.e. under 200-300° C. depending on type and substratum), those having a sterically hindered hydroxyl group as well as the derivatives of dihydroxyaryl compounds the hydroxyl groups of which are in o- or p-position to each other, are suitable. Examples of particularly valuable compounds which can be used are the monophenol derivatives such as 2,4 - dimethyl - 6 - tert. butylphenol, 2,6-di-tert.butyl-4-ethylphenol, 2,6-bis-(1'-methylcyclohexyl) - 4 - methylphenol, 2,6-di-tert.butyl-4-dimethylaminomethyl phenol, 2,2'-methylene-bis-(4-6-tert.butyl phenol), 2,2' - thio - bis - (4-methyl-6-tert. butylphenol), 4,4' - dihydroxy - 2,2' - dimethyl - 5,5' - di-tert.butyl-diphenyl sulphide and diphenyl disulphide, 2,6-bis-(2' - hydroxy - 3' - tert.butyl - 5' - methylbenzyl)-4-methylphenol, derivatives of polynuclear phenols such as 2-tert.butyl-1-hydroxynaphthalene, 4,6-di-tert.butyl-5-hydroxyindane, 5-hydroxyacenaphthene, polyvalent phenols and derivatives thereof: butyl pyrocatechin, octyl gallate, hydroquinone, butylhydroxy anisole, hydroquinone monobenzyl ether.

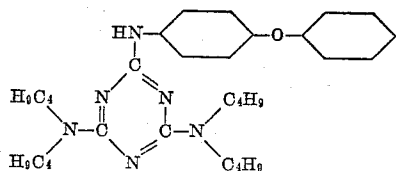
Of the aminohydroxyaryl compounds usable as antioxidants, those derivatives in which the amino and hydroxyl groups are in p-position to each other are particularly suitable. Examples are: p-hydroxydiphenylamine, p-hydroxyoctyl aniline, p-hydroxy-N- γ -aminopropyl aniline.

Of the heterocyclic compounds usable as antioxidants, the cyclic imides are the best known; in addition however, also heterocyclic compounds having no nitrogen can be employed insofar as they are not included in the class of heterocyclic amines. Examples are: phenothiazine, iminodibenzyl, 5-ethyl-10,10-diphenyl-phenosilazine, 6-methoxy- or 6-ethoxy- or 6-ethylamino-2,2,4-trimethyl-1,2-dihydroquinoline or telomers thereof, 3-hydroxy-7,8-benzo-1,2,3,4-tetrahydroquinoline or tocopherol. Also didodecyl selenide and Topanol CA of Imperial Chemical Industries may be used as antioxidants.

The following examples illustrate the particular suitability of the N,N',N''-substituted melamines according to the invention for use as synthetic lubricants, as hydraulic liquids as well as oils for turboprop engines. Measurements are given therein according to the metric system and the temperatures are in degrees centigrade.

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Example 1.—2,4-bis-dibutylamino-6-p-phenoxyphenyl-amino-s-triazine



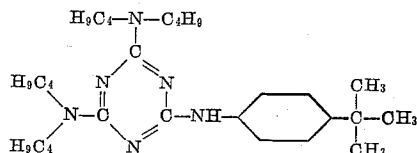
A mixture consisting of 148 parts of 2,4-bisdibutylamino-6-chloro-s-triazine, 129 parts of p-phenoxyamino-benzene and 16 parts of pulverised sodium hydroxide is heated while stirring for 5 hours at 150° and then for 3 hours 45 minutes at 165°. The inorganic components are filtered off and the filtrate is fractionally distilled in vacuo. The desired triazine derivate distills at B.P. >240° under 0.02 mm. pressure (bath temperature 280–290°) without decomposition as a highly viscous liquid.

Yield: 93.4% of the theoretical.

Analysis.— $C_{31}H_{46}N_6O$, M.W. 518. Calculated, percent: C, 71.75; H, 8.88; N, 16.23. Found, percent: C, 71.76; H, 8.82; N, 16.36.

Because of its very good thermostability, its slight volatility which in a test showed that under introduction of nitrogen at atmospheric pressure for 6 hours at 400°, a loss of weight of only 2.7% occurred, as well as its high viscosity, the compound is a valuable lubricant for parts of machines working at higher temperatures.

Example 2.—2,4-bis-dibutylamino-6-p-tert.butylphenylamino-s-triazine



A mixture consisting of 148 parts of 2,4-bis-dibutylamino-6-chloro-s-triazine, 105 parts of p-tert.butylaniline and 16 parts of pulverised sodium hydroxide is heated while stirring for 15 minutes at 100° and then for 8 hours at 140°. The mixture is then diluted with xylene, the inorganic components are filtered off, the filtrate is washed with water, dried and distilled. At B.P. 224–232° under 0.1 mm. pressure, 179 parts of a colourless oil distill. Refraction index n_D^{25} : 1.5432; yield: 97.1% of the theoretical.

Analysis.— $C_{29}H_{50}N_6$, calculated, percent: C, 72.30; H, 10.37; N, 17.43. Found, percent: C, 72.46; H, 10.46; N, 17.47.

Because of the very good thermostability of the compound, its slight volatility which is shown by the loss in weight which, on the introduction of nitrogen at atmospheric pressure for 6 hours at 400°, is only 10%, and because of its favourable medium viscosity and because of the only slight alteration thereof which occurs on heating, this melamine derivative is a suitable oil for turboprop aero engines.

Example 3

3 parts of copper phthalocyanine are stirred in 25 parts by volume of benzene in an "Ultraturax" mixing apparatus (Janke & Kundel, Stauffen, Baden, Germany). 9 parts of 2,4-bis-dibutylamino-6-p-tert.butylphenylamino-1,3,5-triazine are slowly added to this mixture and the whole is then stirred for 45 minutes. The homogeneous mass so obtained is worked on a glass surface with a spatula until the excess benzene has evaporated.

The mass obtained is heated for 45 minutes at 150° and, after cooling, is again worked with a spatula.

A good grease which can be well worked up is obtained.

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Similar results are obtained on using the melamine derivatives given in Table I with the addition of the thickeners usually employed for the particular purpose.

Example 4

99 parts of 2,4-bis-dibutylamino-6-(N-methyl-N-phenylamino)-1,3,5-triazine and 1 part of iminodibenzyl are stirred together until the latter has completely dissolved. The mixture obtained has improved stability to oxidation compared with the pure triazine compound.

Similar results are obtained if antioxidants suitable for the intended use are added in amounts of 0.01 to 5% to the compounds given in Table I. As antioxidants may also be used didodecylselenid or Topanol CA of the Imperial Chemical Company.

Similar results are obtained if the compounds given in Table I are mixed with high pressure additives and antioxidants suitable for the intended use in amounts of 0.01 to 5%.

Example 5

97.5 parts of 2,4-bis-dibutylamino-6-benzylamino-1,3,5-triazine, 1.5 parts of dibutyl phosphite and 1 part of phenyl- α -naphthylamine are mixed well by stirring. Compared with the pure triazine, the mixture formed thus has improved stability to oxidation and better load carrying property.

Similar results are obtained if anticorrosives suitable for the intended use are added in amounts of 0.01 to 2% to the compounds given in Table I.

Example 6

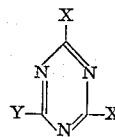
99.8 parts of 2,4-bis-bibutylamino-6-p-phenoxyphenyl-amino-1,3,5-triazine and 0.2 part of benzotriazole are mixed. Compared with the pure triazine, the mixture obtained has a less corrosive action in particular on copper and alloys thereof.

Example 7

97 parts of 2,4-bis-dibutylamino-6-benzylamino-1,3,5-triazine and 3 parts of polymers of methacrylic acid ester, in particular poly-2-ethylhexyl-methacrylate (HF 825, Röhm and Haas Co., Philadelphia U.S.A.) are homogeneously mixed by stirring. This mixture has a lower solidification point than the pure 2,4-bis-dibutylamino-6-benzylamino-1,3,5-triazine.

The choice of polymers as additive reducing the solidification point is advantageously made according to the desired solution in the triazine derivative.

The following Tables I and Ia contain examples of N,N',N''-substituted melamines of the formula



usable according to the invention. They are produced by reacting cyanuric chloride in steps with the primary and secondary organic amines corresponding to X, Y and Z according to the method described in detail in Example 1. Column 5 of Table I shows the yield attained in the last step in percentage of the theoretical, columns 6 and 7 give the boiling point of the compounds under reduced pressure, column 8 shows the refraction index and column 9 the molecular weight of the compounds. Column 2 in Table Ia contains the formulae of the compounds and column 3 and the following columns show the results of elementary analysis for carbon, hydrogen and nitrogen in percent comparison with the theoretical content.

Table II shows the physical data of the compounds from which the suitability of these stable, difficultly volatile melamine derivatives as hydraulic liquids and/or lubricants can be seen. Columns 2 and 3 give the viscosity measured at 100° F. (=37.8° C.) and 210° F.

(=98.8° C.), and column 4 shows the so-called ASTM slope.

The meaning of the ASTM slope is as follows: If in a co-ordinate system, the temperature (in degrees Fahrenheit) is given as the abscissa and the natural log of the viscosity (in centistokes) is given as ordinate, then a plot is formed, which, for practical purposes, can be regarded as straight. Thus the viscosity for the whole tem-

Columns 5 and 6 show the loss in weight in percentage within 6 hours incurred by a sample of 25 cc. on heating to 380° or 400° C. in a glass test tube of about 25 mm. diameter with simultaneous introduction of nitrogen (2 litre per hour).

Column 7 shows the alteration in the viscosity in percentage measured at 210° F. incurred by the sample on heating for 6 hours as described above.

TABLE I

No.	X	Y	Percent	Percent	B.P. at—		η_{25}	MG
					C °	mm. Hg.		
1-----	$N(C_2H_5)_2$	$N(C_2H_5)_2$	$NHCH_2$ 	85.5	180-88	0.01	1.5582	328
2-----	$N(C_4H_9)_2$	$N(C_4H_9)_2$	$NHCH_2$ 	85.0	206-25	0.07	1.5323	440
3-----	$N(C_4H_9)_2$	$N(C_4H_9)_2$	NH  O 	93.4	>240	0.02	1.5500	518
4-----	$N(C_4H_9)_2$	$N(C_4H_9)_2$	NH  $C(CH_3)_2$ 	97.1	224-32	0.1	1.5432	482
5-----	$N(C_4H_9)_2$	$N(C_4H_9)_2$	C_2H_5  N	90.6	194-99	0.06	1.5273	454

TABLE IA

No.		C Percent		Analysis, H Percent			
		Calc.	Found	Calc.	Found	Calc.	Found
1-----	$C_{18}H_{28}N_6$	65.80	65.85	8.55	8.76	25.60	25.52
2-----	$C_{26}H_{44}N_6$	70.9	70.9	10.0	10.14	19.1	19.46
3-----	$C_{31}H_{46}N_6O$	71.75	71.76	8.88	8.82	16.23	16.36
4-----	$C_{29}H_{50}N_6$	72.3	72.46	10.37	10.46	17.43	17.47
5-----	$C_{27}H_{48}N_6$	71.42	71.25	10.12	10.27	18.49	18.60

TABLE II

No.	Viscosity in centistokes at—		ASTM slope	Loss in weight after 6 hours at—		Change in viscosity after 6 hours in centistokes in percent at 210° F.
	100° F. (37.8° C.)	210° F. (98.8° C.)		° C.	Percent	
1-----	317.8	10.87	0.748	380	2.41	+77.5
				400	22.7	+262
2-----	269.2	15.25	0.777	380	3.7	+97.1
				400	12.28	+332.0
3-----	4,117.0	49.94	0.836	380	4.84	+4.6
				400	10.92	+47.7
4-----	15,520	73.31	0.909	380	3.62	+21.6
				400	10.01	+46.0
5-----	218.2	15.83	0.721	380	3.6	+19.9
				400	9.6	+102.4

perature range can be interpolated from two points determined by experiment (conventionally the viscosities at 100° F. and 210° F. are determined). The slope of this plot is a standard for the dependency of the viscosity on temperature. Therefore, the ASTM slope is the quotient of the ordinate over the abscissa of the two points measured in cm. which are obtained by plotting the actual viscosity values at various temperatures in the ASTM chart. The ASTM Standard Viscosity-Temperature Charts for liquid petroleum products (Method D 341) are standard graphs which are in close resemblance to the co-ordinate system described above.

The lower the figure shown for a liquid in this ASTM slope the better suited it is as lubricant. A value of over 1.0 means that the liquid in question is not very suitable. ASTM is an abbreviation for American Society for Testing Materials, 1916 Race Street, Philadelphia, Pa., U.S.A.

The lubricity of a representative composition of matter according to the invention was measured in a Shell 4 ball apparatus. The apparatus was run for 30 minutes at 1450 revolutions per minute under a 40 kg. load and using half inch Grade "A" S.K.F. steel balls. The starting temperature was about 40° C.

The compounds according to the invention can be used direct for the lubrication of solid surfaces.

Example 8

50 parts of 2,4-bis-dibutylamino-6-p-phenoxyphenyl-amino-1,3,5-triazine and 50 parts of dinonyl adipate are stirred. This mixture has a viscosity of 95.0 centistokes at 37.8° and 9.5 centistokes at 98.8°. ASTM slope 0.74.

Example 9

50 parts of 2,4-bis-dibutylamino-6-(N-ethyl-N-phenyl-amino)-1,3,5-triazine and 50 parts of silicone oil DC are

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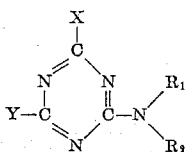
stirred. The mixture has a viscosity of 85.2 centistokes at 37.8° and 16.3 centistokes at 98.8°. ASTM slope 0.50.

The silicone oil DC of the Dow Corning Co. has the following viscosity values:

At 98.8°=17.33 centistokes
At 37.8°=42.24 centistokes.

What is claimed is.

1. A compound of the formula



wherein

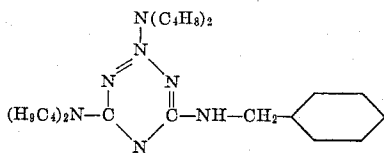
X is a di-(lower alkyl)-amino group in which each alkyl radical has from 2 to 4 carbon atoms

Y is a di-(lower alkyl)-amino group in which each alkyl radical has from 2 to 4 carbon atoms

R₁ is a member selected from the group consisting of hydrogen and lower alkyl of maximally 4 carbon atoms,

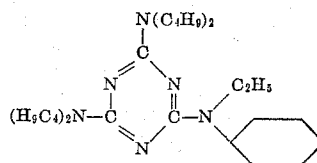
R₂ is a member selected from the group consisting of benzyl, phenyl, alkylphenyl wherein alkyl has maximally 12 carbon atoms, alkoxy-phenyl, wherein alkoxy has maximally 4 carbon atoms and phenoxy-phenyl.

2. A compound of the formula

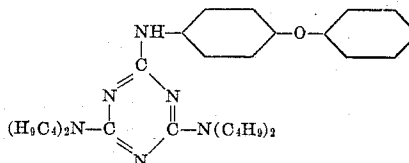


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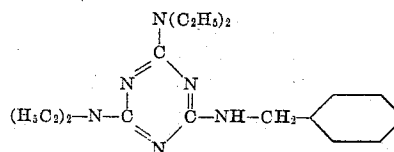
3. A compound of the formula



4. A compound of the formula



5. A compound of the formula



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